

# Correlation Energy Estimators based on Møller-Plesset Perturbation Theory

Herbert H. H. Homeier<sup>1</sup>

*Institut für Physikalische und Theoretische Chemie, Universität Regensburg,  
D-93040 Regensburg, Germany*

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## Abstract

Some methods for the convergence acceleration of the Møller-Plesset perturbation series for the correlation energy are discussed. The order-by-order summation is less effective than the Feenberg series. The latter is obtained by renormalizing the unperturbed Hamilton operator by a constant factor that is optimized for the third order energy. In the fifth order case, the Feenberg series can be improved by order-dependent optimization of the parameter. Alternatively, one may use Padé approximants or a further method based on effective characteristic polynomials to accelerate the convergence of the perturbation series. Numerical evidence is presented that, besides the Feenberg-type approaches, suitable Padé approximants, and also the effective second order characteristic polynomial, are excellent tools for correlation energy estimation.

*Key words:* Many-body perturbation theory, convergence acceleration, extrapolation, Møller-Plesset series, Feenberg series, Padé approximants, effective characteristic polynomials

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## 1 Introduction

Quite often in theoretical work, approximation schemes for some quantities converge rather slowly. Thus, there is a need for means to accelerate convergence or, equivalently, to extrapolate from few members of a sequence to its limit. Fortunately, the development of such methods has become a rather active field at the borderline between mathematics and the sciences in recent years. Brezinski and Redivo Zaglia [1] have given an excellent mathematical introduction to such methods. There are many methods that can be used to

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<sup>1</sup> na.hhomeier@na-net.ornl.gov, <http://rchs1.uni-regensburg.de/%7Ec5008/>

accelerate slowly convergent (or to sum divergent) power series in terms of rational approximations, e.g., Padé approximants [2–4] that are related to the famous epsilon algorithm [5], Levin-type methods [6–9], and iterative methods [10] like the recently developed  $\mathcal{J}$  transformation [11–13]. There are also methods that can be used to accelerate the convergence of Fourier [14,15,8] and other orthogonal series [16,17]. Onedimensional iteration sequences can be accelerated very effectively as is demonstrated in [18] for the case of the inverse Dyson equation. There is also a growing literature on extrapolation of matrix and vector sequences (see [1] for an introduction) that have found applications to the computation of matrix functions [19] and the iterative solution of fixed-point equations [20]. The full potential for application of these methods in the sciences has still to be explored.

One of the fields where these methods may be applied is Many-Body Perturbation Theory (MBPT), that is one of the standard methods to obtain the correlation energy in molecular *ab initio* calculations. The convergence acceleration of many-body perturbation series has recently become a topic of increasing interest [21–27], also in the context of time-dependent phenomena [28]. Here, we restrict attention to approaches to correlation energy estimation that are based on the Møller-Plesset (MP) series since the latter is commonly and routinely used in quantum chemistry for closed-shell systems. For open-shell systems, the restricted MP (RMP) method has been developed [29] that is based on an restricted open-shell Hartree-Fock (ROHF) determination of the MP unperturbed Hamiltonian. In this way, the RMP approach largely avoids spin contaminations that are characteristic for unrestricted MP (UMP) based on an unrestricted HF (UHF) zero-order calculation. For smaller molecules, calculations up to fourth or even fifth order do not pose large problems, and MP<sub>n</sub> (n=2,4) calculations are a popular approach to the correlation problem. However, the computational effort increases steeply with the order of the perturbation series, and with the size of the molecular system. Therefore, there is a need to make the best use of the lower-order terms since higher terms are difficult to obtain. Order-by-order summation of the perturbation expansion as given by

$$E = E_0 + E_1 + E_2 + E_3 + E_4 + E_5 + \dots, \quad (1)$$

i.e., using the  $n$ th order estimate

$$E^{(n)} = \sum_{j=0}^n E_j, \quad (2)$$

is not the best way to exploit the information content of its terms. It has been shown by Schmidt, Warken and Handy [21] that a specific variant of a method originally proposed by Goldhammer and Feenberg [30,31] for the

Brillouin-Wigner perturbation expansion allows to obtain better estimates for the correlation energy than order-by-order summation of the usual MP series. This variant was called the *Feenberg series* in [21]. It is also a special case of the so-called *Geometric Approximation* [32–35]. Similar to the original approach of Goldhammer and Feenberg [30,31], the computation of the Feenberg series requires only the terms  $E_j$  of the perturbation series.

Alternatively, one may use Padé approximants that provide rational approximations  $[p, q]$  to power series, where  $p$  denotes the order of the numerator polynomial, and  $q$  that of the denominator polynomial. Padé approximants may be calculated for the original perturbation series, and also for the renormalized perturbation series. As shown by Wilson, Silver, and Farrell [35], the special Padé approximants  $[n + 1, n]$  have the property that they are invariant under the scaling of the unperturbed Hamilton operator and, thus, are identical for the original and the renormalized case. This invariance is an important property of correlation energy estimators since the true correlation energy is independent of our choice of the unperturbed Hamiltonian.

Recently, a method based on effective characteristic polynomials has been applied to correlation energy computations of some model systems [36–42] and for the summation of perturbation expansions of anharmonic oscillators [43]. We will see that results based on low-order effective characteristic polynomials also have the desirable invariance property under rescaling of the unperturbed Hamiltonian.

All these methods require only the terms  $E_i$  of the Møller-Plesset perturbation series. The additional effort to calculate them besides the usual perturbation series is very low. As will be shown, these methods allow to obtain much better estimates of the correlation energy in many cases, and allow the identification of cases where standard perturbation theory fails. In these cases, computationally more demanding correlation energy estimators have to be used [21–27,44–69].

## 2 Methods

The Goldhammer-Feenberg approach [30,31] renormalizes the unperturbed Hamiltonian  $H_0$  by a constant factor according to

$$H_0(\alpha) = (1 - \alpha)H_0. \quad (3)$$

This leads to a repartitioning of the total Hamiltonian  $H = H_0 + H_1$  as

$$H = H_0(\alpha) + H_1(\alpha), \quad H_1(\alpha) = H_1 + \alpha H_0. \quad (4)$$

It also leads to a renormalized perturbation series

$$E(\alpha) = E_0(\alpha) + E_1(\alpha) + E_2(\alpha) + E_3(\alpha) + E_4(\alpha) + E_5(\alpha) + \dots \quad (5)$$

with partial sums — i.e., renormalized  $n$ th order energy estimates — given by

$$E^{(n)}(\alpha) = \sum_{j=0}^n E_j(\alpha) \quad (6)$$

depending on renormalized  $j$ th order contributions [31, Eq. (12)]

$$\begin{aligned} E_0(\alpha) &= (1 - \alpha)E_0, & E_1(\alpha) &= E_1 + \alpha E_0, \\ E_n(\alpha) &= \frac{1}{(1 - \alpha)^{n-1}} \sum_{j=2}^n \binom{n-2}{j-2} (-\alpha)^{n-j} E_j, & (n \geq 2). \end{aligned} \quad (7)$$

For the Feenberg series, the factor  $\alpha$  is determined by requiring that the third order energy  $E^{(3)}(\alpha)$  of the renormalized perturbation expansion is stationary with respect to variations of the factor  $\alpha$ . This leads to an optimized value based on the third order result given by  $\alpha^{(3)} = E_3/E_2$ . In this way, the partitioning of the Hamiltonian is fixed, and the Feenberg series is obtained as the usual Rayleigh-Schrödinger series for the unperturbed Hamilton operator  $H_0(\alpha^{(3)})$ . The total energies are

$$F_n = E^{(n)}(\alpha^{(3)}) = E^{(n)}(E_3/E_2). \quad (8)$$

The stationarity of the eigenvalue is based on the observation that the exact value of the energy, i.e., the infinite order result should be independent of the value of  $\alpha$  that is used. When applying this to an approximation obtained in some finite order, that value of  $\alpha$  is best where the derivative of the approximation is as small as possible in absolute value, preferably zero. We remark that this is related to the concept of order-dependent mappings as discussed in [70, Sec. 18]. Since order-by-order summation of the  $\alpha$  dependent Rayleigh-Schrödinger expansion leads to the  $n$ th order estimate  $E^{(n)}(\alpha)$  defined in Eq. (6), the optimal value  $\alpha^{(n)}$  of  $\alpha$  in  $n$ th order is determined from the equation ( $n > 1$ )

$$0 = \frac{dE^{(n)}}{d\alpha}(\alpha^{(n)}), \quad \frac{dE^{(n)}}{d\alpha}(\alpha) = (n-1) E_n(\alpha)/(1-\alpha). \quad (9)$$

The second equality here follows from an explicit calculation. A solution of this equation leads to an approximation

$$GF_n = E^{(n)}(\alpha^{(n)}) \quad (10)$$

for the total energy. Thus, in each order of the renormalized perturbation series, different values of  $\alpha$  are chosen. This approach has been proposed already by Feenberg. We will call its results the total *Goldhammer-Feenberg energies* in order to distinguish it from the Feenberg total energies. Obviously, there can be several solutions of Eq. (9), and the Goldhammer-Feenberg energies are not guaranteed to be real.

In the case of fifth order, the condition (9) reduces in combination with Eq. (7) to requiring that  $\alpha^{(5)}$  is a root of the third order polynomial  $(1-\alpha)^4 E_5(\alpha)$ . The latter has real coefficients and, thus, is guaranteed to have a real solution  $\alpha_r^{(5)}$ . The corresponding value  $E^{(5)}(\alpha_r^{(5)})$  will be called GF5 later. Alternatively, one can use the average of the two (in the present case always) complex energies obtained from the other roots of the third order polynomial. This average will be called GF5b later.

As is well-known (see for instance [47,56]), Rayleigh-Schrödinger MBPT is size-extensive order by order, i.e., for a super-molecule build up from  $N$  non-interacting identical systems, the perturbation energies are linear in  $N$  in each order. Thus, if  $E_j$  is the  $j$ th term of the perturbation series of one of the  $N$  subsystems, the  $j$ th order term of the perturbation series for the super-molecule is  $N E_j$ .

In the case of the Feenberg scaling, we note that Eq. (7) implies that for  $E_j \rightarrow N E_j$ , we also have  $E_j(\alpha) \rightarrow N E_j(\alpha)$ . Thus, for any  $\alpha$  that is independent of  $N$ , also the renormalized perturbation series is size-extensive in each order. Since  $\alpha^{(3)} = E_3/E_2$  is invariant under  $E_j \rightarrow N E_j$ , all Feenberg energies  $F_n$  are size-extensive as a consequence of Eq. (8).

The Goldhammer-Feenberg energies  $GF_n$  for  $n > 1$  are also size-extensive. To prove this, we note that under  $E_n \rightarrow N E_n$ , we have  $dE_n/d\alpha \rightarrow N dE_n/d\alpha$ . This follows from the last equality in Eq. (9), since  $E_n(\alpha) \rightarrow N E_n(\alpha)$  under  $E_n \rightarrow N E_n$ . This implies that the positions of the zeros of  $dE_n/d\alpha$ , and hence the positions  $\alpha^{(n)}$  of the extrema of  $E_n(\alpha)$  are invariant under  $E_n \rightarrow N E_n$ . Since the  $\alpha^{(n)}$  are used to define the Goldhammer-Feenberg energies, the latter are size-extensive. In particular, this applies to GF5 and GF5b.

Now, we sketch the method of the effective characteristic polynomial that has recently been applied to the summation of divergent perturbation series [43]. In the linear variation method with  $n$  orthonormal basis functions  $\{\phi_j\}_{j=1}^n$  applied to a Hamiltonian  $H$ , the characteristic polynomial  $P_n(E)$  of degree  $n$  in the unknown energy  $E$  has the form

$$P_n(E) = \det |\langle \phi_j | H | \phi_k \rangle - E \delta_{j,k}| . \quad (11)$$

If  $H = H_0 + \beta V$ , the polynomial has the form ([43], Eq. (3.2))

$$P_n(E) = \sum_{j=0}^n E^j \sum_{k=0}^{n-j} f_{n,j,k} \beta^k \quad (12)$$

with  $f_{n,n,0} = 1$ . Thus,  $N = n(n+3)/2$  coefficients  $f_{n,j,k}$  have to be determined. They could be obtained from the matrix elements of  $H_0$  and  $V$ . In the method of the characteristic polynomial, they are obtained from the coefficients of the perturbation series for  $E$

$$E = \sum_{j=0}^{\infty} E_j \beta^j . \quad (13)$$

For this end, one uses (13) in (12) and does a Taylor expansion in  $\beta$  with the result

$$P_n \left( \sum_{j=0}^{\infty} E_j \beta^j \right) = \sum_{k=0}^{N-1} A_k \beta^k + O(\beta^N) . \quad (14)$$

The  $A_k$  depend on the  $f_{n,j,k}$ . Since  $P_n(E) = 0$  for an eigenvalue  $E$ , one demands

$$A_k = 0 , \quad 0 \leq k \leq N - 1 . \quad (15)$$

This yields a linear equation system for the unknown  $f_{n,j,k}$ , and thus, these coefficients can be determined. After the determination, the effective characteristic equation  $P_n(E) = 0$  is solved for  $E$ . If only perturbation coefficients  $E_j$  up to  $j = 5$  are available, only a second degree effective characteristic polynomial can be used. In our case, one finally puts  $\beta = 1$ . In this way, one obtains an explicit solution of  $P_2(E) = 0$  as

$$\Pi_2 = E_0 + E_1 + \frac{E_2^2}{2} \frac{E_2 - E_3 + \sqrt{(E_2 - E_3)^2 - 4(E_2 E_4 - E_3^2)}}{E_2 E_4 - E_3^2} \quad (16)$$

A further solution (with a minus sign of the square root) only yields the correct result for small  $\beta$  if  $E_2 > 0$  holds which does not occur in perturbation theory calculations of ground states.

Direct calculation shows that the estimate  $\Pi_2$  is independent under a scaling of  $H_0$ , i.e., we have

$$\Pi_2(E_0, \dots, E_4) = \Pi_2(E_0(\alpha), \dots, E_4(\alpha)) . \quad (17)$$

Since the true characteristic polynomials — depending only on the total Hamiltonian — are invariant under Feenberg scaling, it may be conjectured that this invariance also holds for estimates obtained as roots of effective characteristic polynomials of higher degree. A proof of this conjecture is under investigation.

We denote  $\Pi_2$  also as estimate  $\Pi_2$  for the total energy in the following.

It is easy to see from Eq. (16) that  $\Pi_2 \rightarrow N \Pi_2$  if  $E_j \rightarrow N E_j$  for all  $j$  with  $0 \leq j \leq 4$ . Thus, the  $\Pi_2$  estimator is size-extensive.

Padé approximants [2–4] are defined with respect to a given power series as ratios of two polynomials. Given numerator and denominator polynomial degrees  $p$  and  $q$ , the coefficients of these polynomials in the Padé approximant  $[p, q]$  are determined by requiring that up to the order  $p+q$ , the coefficients in the Taylor expansion of the ratio of polynomials are equal to the coefficients of the given power series. In the present contribution, we take as this power series the perturbation expansion (13) in the parameter  $\beta$  that is put equal to one in the final formulas. We note that a different power series that is not explicitly defined, seems to have been used for the Padé approximants in [71]. For the application of rational approximants to the Møller-Plesset series see also Ref. [72].

### 3 Numerical Results

Fortunately, excellent data for the test of the methods described in the previous section are available in [21]. This paper also includes results given in [71]. In these references, a large number of Møller-Plesset results up to fifth order, and FCI (Full Configuration Interaction) or CCSDT (Coupled Cluster Singles Doubles Triples) results are given for the ground states of benchmark molecules (BH, HF, CH<sub>2</sub>, H<sub>2</sub>O, NH<sub>2</sub>, NH<sub>3</sub>, CO, C<sub>2</sub>H<sub>2</sub>, O<sub>3</sub>, CN). The results of the reanalysis of these data is presented in Table 1. For completeness, the MP data are also plotted. If not stated otherwise, MPn means RMPn in open shell cases. Apart from case n (NH<sub>3</sub>), the left half of the data in Table 1 is obtained from the data up to fourth order, while the right half also depends on the fifth order.

It is seen that in many cases, the correlation energy estimators provide excellent results. Problematic cases are s, t, and u. In case s corresponding to CN, the perturbation series is divergent, being based on doubly occupied ROHF orbitals where for alpha and beta spins the same orbitals are used, unlike the RMP orbitals where occupied alpha and beta set both are rotated. [21,66] In cases t and u corresponding to H<sub>2</sub>O at stretched geometries, the approach

is based on an UMP series that is monotonously and very slowly convergent [21,72].

Table 1: Comparison of Correlation Energy Estimators

Method	Energy	%Corr	Method	Energy	%Corr
Case a: BH ( $^1\Sigma$ , $r = 2.329 a_0$ , DZP, [71,73,74])					
SCF	-25.125260	0.00	MP5	-25.225101	97.53
MP2	-25.198988	72.02	F5	-25.226881	99.27
MP3	-25.216566	89.19	GF5	-25.226971	99.36
MP4	-25.222567	95.06	GF5b	-25.227088	99.47
F4	-25.226167	98.57	[3,2]	-25.227299	99.68
[2, 2]	-25.225294	97.72	[2,3]	-25.227478	99.85
II2	-25.226555	98.95	FCI	-25.227627	100.00
Case b: BH ( $^1\Sigma$ , $r = 1.5 \times 2.329 a_0$ , DZP, [71,75])					
SCF	-25.062213	0.00	MP5	-25.172372	96.83
MP2	-25.139869	68.26	F5	-25.174484	98.69
MP3	-25.160249	86.18	GF5	-25.174544	98.74
MP4	-25.168745	93.64	GF5b	-25.177010	100.91
F4	-25.175345	99.45	[3,2]	-25.175078	99.21
[2, 2]	-25.173623	97.93	[2,3]	-25.175106	99.24
II2	-25.176791	100.72	FCI	-25.175976	100.00
Case c: BH ( $^1\Sigma$ , $r = 2 \times 2.329 a_0$ , DZP, [71,75])					
SCF	-24.988201	0.00	MP5	-25.121278	95.65
MP2	-25.074503	62.03	F5	-25.126844	99.65
MP3	-25.100221	80.51	GF5	-25.126983	99.75
MP4	-25.114005	90.42	GF5b	-25.130104	101.99
F4	-25.128829	101.08	[3,2]	-25.129407	101.49
[2, 2]	-25.124953	98.29	[2,3]	-25.129475	101.54
II2	-25.137084	107.01	FCI	-25.127333	100.00
Case d: HF ( $r = 1.733 a_0$ , DZP, [71,76])					



(Table 1 – continued)

SCF	-100.047087	0.00	MP5	-100.250158	99.60
MP2	-100.243165	96.17	F5	-100.250099	99.57
MP3	-100.245531	97.33	GF5	-100.250276	99.66
MP4	-100.251232	100.13	GF5b	-100.251988	100.50
F4	-100.251443	100.23	[3,2]	-100.250468	99.75
[2, 2]	-100.251547	100.28	[2,3]	-100.250481	99.76
II2	-100.251820	100.42	FCI	-100.250969	100.00
Case e: HF ( $r = 1.5 \times 1.733 a_0$ , DZP, [71,76])					
SCF	-99.933230	0.00	MP5	-100.158121	99.00
MP2	-100.149756	95.32	F5	-100.158152	99.01
MP3	-100.148543	94.78	GF5	-100.158247	99.05
MP4	-100.159627	99.66	GF5b	-100.161609	100.53
F4	-100.159443	99.58	[3,2]	-100.158750	99.28
[2, 2]	-100.160091	99.87	[2,3]	-100.158757	99.28
II2	-100.160708	100.14	FCI	-100.160395	100.00
Case f: HF ( $r = 2 \times 1.733 a_0$ , DZP, [71,76])					
SCF	-99.817571	0.00	MP5	-100.073004	96.93
MP2	-100.057062	90.88	F5	-100.073139	96.98
MP3	-100.054148	89.77	GF5	-100.073301	97.04
MP4	-100.076267	98.16	GF5b	-100.079678	99.46
F4	-100.075480	97.86	[3,2]	-100.075064	97.71
[2, 2]	-100.077899	98.78	[2,3]	-100.075072	97.71
II2	-100.080476	99.76	FCI	-100.081107	100.00
Case g: CH <sub>2</sub> ( $^1A_1$ , $r = 2.11 a_0$ , $\theta = 102.4^\circ$ , DZP, [71,77])					
SCF	-38.886297	0.00	MP5	-39.024234	97.91
MP2	-38.996127	77.96	F5	-39.025336	98.69
MP3	-39.016593	92.48	GF5	-39.025450	98.77
MP4	-39.022203	96.47	GF5b	-39.025413	98.74

(Table 1 – continued)

F4	-39.024615	98.18	[3,2]	-39.025674	98.93
[2, 2]	-39.024049	97.78	[2,3]	-39.025895	99.09
Π2	-39.024791	98.30	FCI	-39.027183	100.00
Case h: H <sub>2</sub> O ( <sup>1</sup> A <sub>1</sub> , $r = 1.88973 a_0$ , $\theta = 104.5^\circ$ , DZP, [71,78])					
SCF	-76.040542	0.00	MP5	-76.255924	99.68
MP2	-76.243660	94.00	F5	-76.255918	99.67
MP3	-76.249403	96.66	GF5	-76.255929	99.68
MP4	-76.255706	99.58	GF5b	-76.257338	100.33
F4	-76.256262	99.83	[3,2]	-76.256134	99.77
[2, 2]	-76.256282	99.84	[2,3]	-76.256135	99.77
Π2	-76.256729	100.05	FCI	-76.256624	100.00
Case i: H <sub>2</sub> O ( <sup>1</sup> A <sub>1</sub> , $r = 1.5 \times 1.88973 a_0$ , $\theta = 104.5^\circ$ , DZP, [71,78])					
SCF	-75.800494	0.00	MP5	-76.066422	98.16
MP2	-76.048095	91.40	F5	-76.066368	98.14
MP3	-76.045081	90.28	GF5	-76.066442	98.17
MP4	-76.065641	97.87	GF5b	-76.068395	98.89
F4	-76.064909	97.60	[3,2]	-76.068528	98.94
[2, 2]	-76.066937	98.35	[2,3]	-76.068533	98.94
Π2	-76.068954	99.10	FCI	-76.071405	100.00
Case j: H <sub>2</sub> O ( <sup>1</sup> A <sub>1</sub> , $r = 2 \times 1.88973 a_0$ , $\theta = 104.5^\circ$ , DZP, [71,78])					
SCF	-75.582286	0.00	MP5	-75.935304	95.41
MP2	-75.898603	85.50	F5	-75.934525	95.20
MP3	-75.877664	79.84	GF5	-75.935353	95.43
MP4	-75.937410	95.98	GF5b	-75.923566	92.24
F4	-75.927115	93.20	[3,2]	-75.949379	99.22
[2, 2]	-75.941045	96.97	[2,3]	-75.949401	99.22
Π2	-75.954930	100.72	FCI	-75.952269	100.00
Case k: NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> , $r = 1.013 \text{ \AA}$ , $\theta = 103.2^\circ$ , 6-31G, [72,29])					

(Table 1 – continued)

SCF	-55.530177	0.00	MP5	-55.632426	99.18
MP2	-55.617272	84.48	F5	-55.632818	99.56
MP3	-55.627501	94.40	GF5	-55.632834	99.57
MP4	-55.631220	98.01	GF5b	-55.633280	100.00
F4	-55.632525	99.27	[3,2]	-55.633011	99.74
[2, 2]	-55.632204	98.96	[2,3]	-55.633022	99.75
II2	-55.632825	99.56	FCI	-55.633276	100.00
Case l: NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> , $r = 1.5 \times 1.013 \text{ \AA}$ , $\theta = 103.2^\circ$ , 6-31G, [72,29])					
SCF	-55.367729	0.00	MP5	-55.520522	96.14
MP2	-55.489967	76.91	F5	-55.521721	96.89
MP3	-55.504270	85.91	GF5	-55.521724	96.90
MP4	-55.516470	93.59	GF5b	-55.523319	97.90
F4	-55.521456	96.73	[3,2]	-55.523696	98.14
[2, 2]	-55.521125	96.52	[2,3]	-55.523706	98.14
II2	-55.526202	99.71	FCI	-55.526658	100.00
Case m: NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> , $r = 2 \times 1.013 \text{ \AA}$ , $\theta = 103.2^\circ$ , 6-31G, [72,29])					
SCF	-55.181593	0.00	MP5	-55.418215	91.36
MP2	-55.357617	67.96	F5	-55.420149	92.11
MP3	-55.375463	74.85	GF5	-55.420173	92.12
MP4	-55.409165	87.87	GF5b	-55.412429	89.13
F4	-55.421427	92.60	[3,2]	-55.432093	96.72
[2, 2]	-55.426946	94.73	[2,3]	-55.432101	96.72
II2	-55.478348	114.58	FCI	-55.440593	100.00
Case n: NH <sub>3</sub> ( $r = 1.91165 a_0$ , $\theta = 106.7^\circ$ , DZ, [73,74])					
SCF	-56.165931	0.00	F4	-56.291937	99.47
MP2	-56.277352	87.95	[2, 2]	-56.291782	99.35
MP3	-56.285281	94.21	II2	-56.292636	100.02
MP4	-56.290692	98.48	FCI	-56.292612	100.00

(Table 1 – continued)

Case o: CO ( $^1\Sigma$ , DZ, [71])					
SCF	-112.760093	0.00	MP5	-113.059117	98.36
MP2	-113.045824	93.99	F5	-113.059254	98.41
MP3	-113.044659	93.61	GF5	-113.060859	98.93
MP4	-113.067749	101.20	GF5b	-113.073579	103.12
F4	-113.067469	101.11	[3,2]	-113.062479	99.47
[2, 2]	-113.069566	101.80	[2,3]	-113.062539	99.49
$\Pi$ 2	-113.072074	102.62	CCSDT	-113.064100	100.00
Case p: C <sub>2</sub> H <sub>2</sub> ( $^1\Sigma_g$ , DZP, [71])					
SCF	-76.831819	0.00	MP5	-77.118892	102.18
MP2	-77.085307	90.23	F5	-77.120192	102.65
MP3	-77.097232	94.47	GF5	-77.122141	103.34
MP4	-77.111732	99.63	GF5b	-77.117205	101.58
F4	-77.113928	100.42	[3,2]	-77.127079	105.10
[2, 2]	-77.114110	100.48	[2,3]	-77.127731	105.33
$\Pi$ 2	-77.116235	101.24	CCSDT	-77.112760	100.00
Case q: O <sub>3</sub> ( $^1A_1$ , DZP, [71])					
SCF	-224.295920	0.00	MP5	-224.929902	97.54
MP2	-224.931924	97.86	F5	-224.933812	98.15
MP3	-224.888104	91.11	GF5	-224.934513	98.25
MP4	-224.952784	101.07	GF5b	-224.952167	100.97
F4	-224.941418	99.32	[3,2]	-224.938301	98.84
[2, 2]	-224.950280	100.68	[2,3]	-224.938367	98.85
$\Pi$ 2	-224.952387	101.00	CCSDT	-224.945859	100.00
Case r: CN ( $^2\Sigma$ , $r = 1.1619$ Å, STO-3G, RMP [29])					
SCF	-90.99752	0.00	MP5	-91.16157	95.07
MP2	-91.15437	90.90	F5	-91.16165	95.12
MP3	-91.14799	87.20	GF5	-91.16166	95.12

(Table 1 – continued)

MP4	-91.16300	95.90	GF5b	-91.16360	96.24
F4	-91.16133	94.93	[3,2]	-91.16297	95.88
[2, 2]	-91.16321	96.02	[2,3]	-91.16297	95.88
II2	-91.16426	96.63	FCI	-91.17008	100.00

Case s: CN ( $^2\Sigma$ ,  $r = 1.1619 \text{ \AA}$ , STO-3G, Hubac-Carsky, [66,79])

SCF	-90.99752	0.00	MP5	-91.12039	71.20
MP2	-91.17762	104.37	F5	-91.15212	89.59
MP3	-91.14160	83.50	GF5	-91.15998	94.15
MP4	-91.19422	113.99	GF5b	-91.18190	106.85
F4	-91.17389	102.21	[3,2]	-91.16350	96.19
[2, 2]	-91.18753	110.11	[2,3]	-91.16359	96.24
II2	-91.19152	112.42	FCI	-91.17008	100.00

Case t: H<sub>2</sub>O ( $r = 1.5 \times 0.967 \text{ \AA}$ ,  $\theta = 107.6^\circ$ , 6-21G,[72])

RHF	-75.707206	0.00	UMP5	-75.853895	76.41
UHF	-75.735012	14.48	F5	-75.855560	77.28
UMP2	-75.829388	63.65	GF5	-75.856608	77.82
UMP3	-75.836823	67.52	GF5b	-75.850870	74.84
UMP4	-75.848211	73.45	[3,2]	-75.862349	80.81
F4	-75.851276	75.05	[2,3]	-75.862421	80.85
[2, 2]	-75.851994	75.42	FCI	-75.899180	100.00
II2	-75.857074	78.07			

Case u: H<sub>2</sub>O ( $r = 2 \times 0.967 \text{ \AA}$ ,  $\theta = 107.6^\circ$ , 6-21G,[72])

RHF	-75.491406	0.00	UMP5	-75.763370	90.72
UHF	-75.699298	69.35	F5	-75.763704	90.83
UMP2	-75.754669	87.82	GF5	-75.763826	90.88
UMP3	-75.760219	89.67	GF5b	-75.763657	90.82
UMP4	-75.762422	90.41	[3,2]	-75.764089	90.96
F4	-75.763098	90.63	[2,3]	-75.764104	90.97

(Table 1 – continued)

[2, 2]	-75.762941	90.58	FCI	-75.791180	100.00
$\Pi 2$	-75.763281	90.69			

Apart from these problematic cases, it is seen that in case m corresponding to  $\text{NH}_2$  at twice the equilibrium distances, the errors are rather high. Excluding this case also, one may study the performance of the correlation energy estimators statistically as shown in Table 2. Plotted are the maximal error, the mean absolute error, the root mean square (rms) absolute error, and the mean percentage of the correlation energy as obtained with the various methods. In cases o, p, and q corresponding to the molecules  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{O}_3$ , respectively, no FCI result is available. The statistical comparison is done once excluding these cases, and once including these cases where as reference for the error calculation the CCSDT result is taken. For these cases, the given correlation energies should thus be taken with care. Carefully designed fourth order methods like  $\Pi 2$  yield correlation energy estimates that can compete with fifth order results. As regards the fifth order methods, it seems that the Goldhammer-Feenberg estimator GF5 is slightly superior to the Feenberg energy F5, and the somewhat *ad hoc* estimator GF5b performs surprisingly well. Among the Padé approximants, the  $[3, 2]$  approximant (that is invariant under the Feenberg scaling) is a rather successful correlation estimator while the  $[2, 3]$  approximant performs very similarly. Other Padé approximants (not displayed in Table 1) do not perform as well as the ones given in this table when applied to the same data.

A careful analysis of the data in Table 1 reveals that the correlation energy estimation based on MP perturbation theory is the better the closer one is to the optimal geometries of the molecule under consideration. This is not very much surprising since it is well-known that the quality of the MP series deteriorates with increasing separations from the equilibrium geometries. Compare for instance the triples of cases (a,b,c) for  $\text{BH}$ , (d,e,f) for  $\text{HF}$ , (h,i,j) for  $\text{H}_2\text{O}$ , and (k,l,m) for  $\text{NH}_2$ , with ratios 1:1.5:2 of the relevant distances. The values away from the equilibrium geometries may or may not be reliable. The data, however, suggest that then the correlation energy estimates are reliable if — as in cases f for  $\text{HF}$  at  $2 \times r_e$  and i for  $\text{H}_2\text{O}$  at  $1.5 \times r_e$  — the values of  $\Pi 2$ , F4 and  $[2, 2]$  do not differ too much from each other. In this situation, the  $\Pi 2$  estimator seems to provide the best results. On the other hand, large differences between the estimates  $\Pi 2$ , F4 and  $[2, 2]$  — as in the cases j for  $\text{H}_2\text{O}$  at  $2 \times r_e$  and m for  $\text{NH}_2$  at  $2 \times r_e$  — clearly indicate that in these cases more sophisticated methods (for instance the  $\Lambda$  transformation [21–27] or multi-reference methods [51,56,69,80–83]) are needed to calculate the correlation energies reliably. As regards the fifth order estimates, it is similarly

Table 2

Statistical comparison of various correlation energy estimators

Method	max $ error $	mean $ error $	rms $ error $	mean %Corr
Sampling 14 cases (a-l,n,r)				
F4	0.02515	0.00433	0.00767	98.3
[2, 2]	0.01122	0.00319	0.00433	98.3
II2	0.00975	0.00199	0.00329	100.1
Sampling 17 cases (a-l,n-r)				
F4	0.02515	0.00409	0.00710	98.6
[2, 2]	0.01122	0.00329	0.00430	98.8
II2	0.00975	0.00269	0.00398	100.3
Sampling 13 cases (a-l,r)				
F5	0.01774	0.00407	0.00628	98.2
GF5	0.01692	0.00394	0.00607	98.2
GF5b	0.02870	0.00400	0.00834	99.0
[3, 2]	0.00711	0.00228	0.00308	99.1
[2, 3]	0.00711	0.00224	0.00307	99.1
Sampling 16 cases (a-l,o-r)				
F5	0.01774	0.00483	0.00678	98.5
GF5	0.01692	0.00470	0.00664	98.6
GF5b	0.02870	0.00452	0.00811	99.6
[3, 2]	0.01432	0.00332	0.00492	99.4
[2, 3]	0.01497	0.00332	0.00503	99.5

seen that a large spread of the values of the various estimates reveals that the MP based methods do not provide sufficiently accurate results. Reversely, a small spread of the various estimates indicates that with a high probability, the (R)MP based correlation energy estimates are reliable.

Comparing fourth and fifth order based estimators, it is seen that the latter do not always provide better estimates of the correlation energy. In many cases, the II2 estimate that is based on fourth order, provides results of comparable quality.

In Tables 3 and 4 the correlation energy estimators are used to calculate the dissociation barrier for  $\text{H}_2\text{CO} \longrightarrow \text{H}_2 + \text{CO}$ , and the barrier height and the heat of reaction for  $\text{CH}_3 + \text{C}_2\text{H}_4 \longrightarrow \text{C}_3\text{H}_7$ .

Table 3

Dissociation barrier (kJ/mol) of  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$  using a TZ2P basis at MP2 geometries <sup>a</sup>

Method	Minimum	Transition state	Barrier	Ref.
SCF	-113.912879	-113.748693	431.1	[21]
MP2	-114.329202	-114.182435	385.3	[21]
MP3	-114.334186	-114.185375	390.7	[21]
MP4	-114.359894	-114.219892	367.6	[21]
F4	-114.360838	-114.220603	368.2	[21]
[2, 2]	-114.362267	-114.223409	364.6	This work
Π2	-114.364840	-114.227767	359.9	This work
BE <sup>b</sup>			360	[84]

<sup>a</sup> [21]

<sup>b</sup> Best estimate [84]

Table 4

Barrier height and heat of reaction (kJ/mol) for  $\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_7$  with a 6-31G\* basis<sup>a</sup>

Method	Reactants	TS <sup>b</sup>	Product	Barrier	HR <sup>c</sup>
RHF	-117.585674	-117.553736	-117.626572	83.8	-107.4
RMP2	-117.967150	-117.952092	-118.014126	39.5	-123.3
RMP3	-118.004259	-117.986543	-118.049999	46.5	-120.1
RMP4	-118.022888	-118.008072	-118.066816	38.9	-115.3
F4	-118.028674	-118.014137	-118.071720	38.2	-113.0
[2, 2]	-118.027529	-118.013226	-118.070703	37.6	-113.3
Π2	-118.030923	-118.017302	-118.073432	35.8	-111.6
exp. <sup>d</sup>				33.1	-107

<sup>a</sup> [21]

<sup>b</sup> Transition state

<sup>c</sup> Heat of reaction

<sup>d</sup> [85–87,21]

In both examples, the calculation is based on known Møller-Plesset energies up to fourth order [21, Tab. 2-4]. The results show that reliable correlation energy estimates as provided by the Feenberg energy F4 [21], the Padé approximant [2, 2], and the effective characteristic polynomial estimate Π2 lead to good agreement with experimental data. The Π2 estimator yields in both cases the best results.

In summary, it has been shown that the availability of various estimators



based on (R)MP results allows in many cases the accurate calculation of the correlation energy at negligible additional computational costs. Also, larger deviations between the values indicate clearly cases where further work is necessary.

Finally, we note that the above estimators are expected to be useful to improve convergence of perturbation series for the energies also for the multi-reference case. This conjecture is a promising topic for further investigations.

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